

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO COSMETIC COMPOSITIONS

- (71) We, GAF CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51st Street, City, County and State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to the use of certain half esters of poly(butyl vinyl ether/maleic anhydride) as film-forming resins in hair and similar cosmetic preparations such as aerosol air sprays, hair conditioners and hair setting lotions. More particularly, the present invention relates to the use of the methyl or ethyl half ester of poly(*n* - butyl or isobutyl vinyl ether/maleic anhydride) as the film-forming resin in hair and similar cosmetic preparations. These resins have excellent adhesion and holding power and also do not have an objectional odour.
- A number of synthetic polymers are currently being used as film-forming agents in hair sprays, hair wave set lotions, hair conditioners, etc., the function of these synthetic polymers being generally to contribute body and holding power to the hair-do sets. Although the holding phenomena of hair sprays and hair setting lotions are not very well defined, it is thought that in hair sprays a polymer globule holds several keratin fibres together so as to produce the necessary holding of the hair in place. Similarly, in setting and conditioning lotions, the polymers are deposited over the surface of the hair and again several hair strands are adhered together. In both the above cases it can be seen that polymer adhesion to the hair is a very important factor which influences the usefulness of a particular synthetic polymer or resin in a hair preparation.
- In addition to good adhesion and holding properties, for a hair spray resin to be truly effective, it must also not be too stiff so as not to give the hair-do an unnatural look.
- Many of the synthetic polymers or resins which are currently employed in hair sprays, wave-set lotions, hair conditioners, etc. form films which are much too hard and thereby give the hair a stiff, unnatural look. In addition, these synthetic polymers and resins sometimes result in excessive flaking or flyaway and make compositions containing these resins unsatisfactory from a commercial point of view. Another desirable property for a synthetic polymer or resin which is to be employed as film-forming agent for use in hair sprays, wave-set lotions, hair conditioners, etc. is humidity stability, i.e., the ability to hold hair even at high humidity levels. Some of the synthetic polymers or resins which provide a more natural look do not have a satisfactory holding power at high humidity levels and therefore are unacceptable for use in those portions of the country which are characterized by high relative humidity levels.
- Although there are some synthetic polymers and resins which have all the above properties, namely, high adhesion and holding power, humidity stability, and a natural look, many otherwise useful compounds have the aesthetically undesirable properties of a hair stiffening effect and a deleterious odour. Since these compounds are to be used in cosmetic preparations, odour is a very important property of the film-forming agents. This has created de-

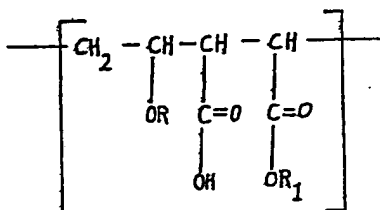
mand for the development of synthetic polymers and resins which have the desirable attributes of good hair spray polymers and are free from the deleterious odour of many synthetic resins and polymers previously used.

It has now been discovered that methyl and ethyl half esters of poly(*n* - butyl or *isobutyl* vinyl ether/maleic anhydride) are useful as film-forming agents in hair sprays, wave-set lotions, hair conditioners, and that these synthetic resins have outstanding humidity stability and hair-holding properties without any aesthetically offensive odour.

The present invention provides cosmetic compositions comprising the methyl or ethyl half esters of poly(*n* - butyl or *isobutyl* vinyl ether/maleic anhydride) as the film-forming resin, and a process for spraying hair using such compositions. The methyl and ethyl half esters of poly(*n*-butyl or *isobutyl* vinyl ether/maleic anhydride) exhibit an improved substantivity to the hair, i.e., these resins are adsorbed onto the keratin surface at least as uniformly and continuously as those synthetic resins and polymers which exhibit all the desirable properties of hair spray resins except for their odour, such as alkyl monoesters of poly(methyl vinyl ether/maleic acid). In addition to these desirable properties, the methyl or ethyl half esters of poly(*n*-butyl or *isobutyl* vinyl ether/maleic anhydride) have an acceptable odour. This is important as these film-forming resins are used in commercial cosmetic formulations, such as hair sprays, wave setting lotions and hair conditioners. If compounds with an undesirable odour are used, perfumes and other odorants must be used in large quantities to cover up the odour.

By employing a polymer without objectionable odour, a hair care preparation compounded without the use of large amounts of fragrance can be prepared. This gives a considerable economic advantage over prior art film-forming resins, since expensive perfumes do not have to be used to mask the final product. The compositions are also stable on storage.

The synthetic polymers and resins which are used in the compositions and improved process of this application have the repeating general formula:



wherein R is *n* - butyl or *iso*-butyl, and R₁ is methyl or ethyl.

The half esters of this invention can be prepared by the esterification of either poly(*n* - butyl vinyl ether/maleic anhydride) or poly(*isobutyl* vinyl ether/maleic anhydride) with either ethyl or methyl alcohol. The base resins which are useful for the production of the novel half esters of this application, i.e., *n* - butyl vinyl ether/maleic anhydride copolymer or *isobutyl* vinyl ether/maleic anhydride copolymer, can be prepared by free radical copolymerization.

In general to serve as a base resin for the half esters of this invention, the *n* - butyl or *isobutyl* vinyl ether/maleic anhydride copolymer preferably has a specific viscosity in a range of from 0.1 to 3.0, as determined on a solution of 1 gram of the copolymer and 100 ml of methyl ethyl ketone at 25°C. The more preferred range of specific viscosity is from 0.1 to 1.0. Resins produced by the method briefly outlined above has a relative viscosity in the range desired.

As stated above, the half esters of *n*-butyl or *isobutyl* vinyl ether/maleic anhydride copolymer may be prepared by the reaction of the base resin with excess ethanol or methanol, which functions both as the solvent and the reactant, with or without the use of a catalyst.

A number of half esters of *n*-butyl or *isobutyl* vinyl ether/maleic anhydride copolymer were prepared and tested. However, only the half methyl and ethyl esters showed good hair holding properties. Higher esters are unsuitable for hair spray applications, because the films formed by these resins are too soft. Although either the methyl or ethyl half esters of the *n* - butyl or *isobutyl* vinyl ether/maleic anhydride copolymers may be used in the composition of this application, the ethyl half ester is preferred.

The copolymers of the present invention are soluble as is in alcohol and when neutralized they are soluble in water and thus can be employed in hair sprays and similar cosmetic compositions containing an alcoholic, aqueous, or mixed alcoholic aqueous base.

A further advantage of the use of the half esters of *n* - butyl or *isobutyl* vinyl ether/maleic anhydride copolymer in hair setting and similar cosmetic preparations is that hair sprayed or otherwise treated with a hair setting composition containing the half esters of this invention is easy to comb and easy to roll on rollers. In addition, setting and conditioning lotions prepared using the half esters of this invention give a firm and stiff curl yet allow easy combing without comb drags.

As indicated above, the half esters of this invention are directly soluble in alcohol and when neutralized are soluble in water. Neutralization is by the addition of an equivalent weight or percentage thereof of an alkaline material to chemically neutralize the unesterified carboxylic acid moiety of the *n*-butyl

or *isobutyl* vinyl ether/maleic anhydride copolymer. Neutralization is advantageous since it increases the water-solubility of the half esters useful in the novel compounds of this invention. Although any alkaline compound may be used to neutralize the half esters useful in the compositions of this application, the following hydroxy substituted alkyl amine type neutralizing agents are preferred: amino methyl propanol, amino methyl propane diol and triisopropanol amine. It should also be noted that if an unneutralized half ester is used in a hair spray composition, soap and water or an alkaline shampoo can easily remove the dry film from the hair.

As indicated above, for hair spray compositions, the base vehicle can be either aqueous, alcoholic, or a mixture of alcohol and water. The alcohol which is used for the alcoholic base or a portion of the water-alcohol solvent system is generally a lower monohydric aliphatic (C_1 — C_8) alcohol, e.g., ethanol, isopropanol, or *n* - propanol, with ethanol being preferred. Thus, the alcoholic solvent can be a commercially and industrially available ethyl alcohol or any one of the denatured alcohol formulations which are permitted by law for use in hair spray preparations, i.e., any of those listed for this use in "Formulas for Denatured Alcohol: Part 212, Title 26 CFR, IRS publication 368. Representative formulations having current approval that can be used are, for example: SDA—40 which consists of 100 gallons of ethyl alcohol denatured with 1.5 ounces of barium sulphate and one-eighth gallon of *tertiary* butyl alcohol; SDA—23 which consists of ten gallons of acetone in each one hundred gallons of ethyl alcohol; and SDA—23 H which consists of eight gallons of methyl *iso*-butyl ketone in each one hundred gallons of ethyl alcohol.

In addition to the film-forming half esters of the *n*-butyl or *isobutyl* vinyl ether/maleic anhydride copolymer and the solvent present in the system, the hair spray or similar composition may contain minor amounts of other ingredients for their usual purposes, for example, wetting agents, defoamers, antibiotic agents, colouring materials, and other suitable additives which are soluble in the aqueous, alcoholic, or mixed solvent medium. Perfumes may also be added, but a much smaller amount is necessary since the film-forming resins do not have an unpleasant odour which must be covered up.

When the aqueous, alcoholic, or mixed solvent system containing the novel composition of this invention is utilized as a spray formulation, the usual aerosol-type container and equipment and usual aerosol-type propellant may be effectively utilized. An alcoholic solution of the resins of this invention is compatible with all the commercially and commonly used propellants. Thus, the propellant may be any material which can be suitably

utilized to propel compositions on to the hair, such as liquefied lower hydrocarbons such as propane, *n* - butane, and *isobutane* and the low boiling chlorofluoro hydrocarbons broadly identified as "Freons" and their commercial equivalents. Thus, for example, mention should be made of "Freon" 11 (trichlorofluoromethane, "Freon" 12 (dichlorodifluoromethane) and "Freon" 114 (1,2 - dichloro - 1,1,2,2 - tetrafluoroethane), and mixtures of these. "Freon" is a Trade Mark.

In an aerosol-type hair spray composition, in accordance with the present invention, the propellant is generally employed in an amount of from 25% to 65% by weight based on the total composition in the container. The film-forming half ester constitutes from 0.1% to 5% by weight with the remainder constituting the alcohol, water, or water-alcohol mixture. In addition, the hair spray composition will usually contain minor amounts, i.e., up to about 5% by weight of a surfactant and still lesser amounts of perfume.

In accordance with a preferred embodiment of the present invention, the sprayable hair composition is generally formed as an alcoholic or mixed aqueous-alcoholic solvent system. Accordingly, suitable amounts of the various components in such a composition are as follows:

Component	Amount	
Half ester film forming resin	0.1—5%	
Alcohol	30 —70%	
Propellant	25 —65%	100
water	0 —25%	

The use of the solvent system and propellant is conventional in the aerosol spray art.

Improved setting and conditioning lotions for the hair can also be provided by the employment of a minor amount, i.e., 0.1%—5% by weight, of the film-forming half esters of *n* - butyl or *isobutyl* vinyl ether/maleic anhydride copolymer in the presence of an aqueous or mixed aqueous and alcoholic system. A setting and conditioning lotion usually includes the following component:

Component	Amount	
Film-forming half ester	0.1—5%	
Water	60 —90%	115
Alcohol	0 —35%	

For use in setting and conditioning lotions, it is preferred in accordance with the present invention to employ a higher molecular weight half ester of *n*-butyl or *isobutyl* vinyl ether/maleic anhydride copolymer. It should also be noted that since a water/base system is to be used, the half esters of *n* - butyl or *iso*-

butyl vinyl ether/maleic anhydride copolymer should be neutralized as indicated above to increase their water solubility. If the amine type neutralizing compounds are used, these compounds provide a creamy lotion consistency to the composition. This is true even when employed in a minor amount of 0.1—5% by weight as set forth above. Gel-forming agents may be added when a gel-like consistency is required. Gel-forming agents include methyl cellulose, CMC, natural gums and polyvinyl pyrrolidone and alkylated polyvinylpyrrolidone.

As was the case with the aerosol hair spray compositions, the setting and conditioning lotions may contain minor amounts of other optional conventional materials. These include such materials as preservatives, additional organic solvents, lanolin and lanolin derivatives and silicone lubricity agents. Here again all these optional components are conventional and employed in minor amounts, i.e., less than 2% by weight. Perfumes may also be optionally added in small amounts since there is no or little odour to cover up.

As disclosed above, the film-forming half esters of *n*-butyl and *iso*-butyl vinyl ether/maleic anhydride copolymer are soluble in both the alcoholic and aqueous systems utilized in the preparations. In order to produce such formulations, it is merely necessary to dissolve the copolymer in the suitable solvent with previous, simultaneous or subsequent addition of other optional components. Solution of the copolymer in the solvent system may be facilitated by mixing.

The novel compositions and improved process of the present invention will be illustrated by the following specific Examples.

EXAMPLE 1.

Preparation of the Resin Base *Isobutyl Vinyl Ether/Maleic Anhydride Copolymer*

A solution was prepared by dissolving 0.9 grams of poly(methoxyethoxyethyl vinyl ether) having a K value of 45 and 0.15 gram of lauroyl peroxide in 100 millilitres of benzene. This solution was added to a 500 ml resin kettle equipped with stirrer, condenser, thermometer and pressure equalized dropping funnel. Air was purged from the kettle by successive evacuation and filling with nitrogen. After establishing a slight positive nitrogen pressure, the temperature was raised to 70°C. and 25 mls of a solution made by dissolving 48 grams of *isobutyl vinyl ether*, 5% excess, and 44.5 grams of maleic anhydride in 200 mls of benzene was added. After waiting 15 minutes and allowing the temperature to reach 75°C., the remainder of the solution was added over one and one-half hours. The test for maleic anhydride was negative 15 minutes after addition was complete.

After cooling to room temperature, the benzene was evaporated from the slurry under re-

duced pressure and the fine white powder placed in a vacuum oven to constant weight. Dry weight of the product was 85 grams.

The *n*-butyl vinyl ether/maleic anhydride copolymer was prepared in a similar manner substituting 48.0 grams of *n* - butyl vinyl ether for the *isobutyl vinyl ether* used above.

EXAMPLE 2.

Preparation of the Half Ethyl Ester of Poly(*Isobutyl Vinyl Ether/Maleic Anhydride*)

A ten liter flask equipped with an air-driven turbine agitator, reflux condenser, and nitrogen inlet was charged with 4000 grams of poly(*isobutyl vinyl ether/maleic anhydride*) and 4921 grams of SD A—40 denatured ethyl alcohol and 10 grams of lithium carbonate. The flask was evacuated and enough nitrogen was introduced to maintain a positive nitrogen pressure throughout the reaction. The mixture was heated to 75°C. and maintained at that temperature for five hours. A sample taken showed by infra-red analysis that all the anhydride had been converted to the half ester.

EXAMPLE 3.

Preparation of the Half Ethyl Ester of Poly(*n*-Butyl Vinyl Ether/Maleic Anhydride)

The reaction procedure according to Example 2 with the exception that 4000 grams of poly(*n* - butyl vinyl ether/maleic anhydride) was substituted for the poly(*isobutyl vinyl ether/maleic anhydride*) used in Example 2. After five hours reaction time, the sample taken showed by infrared analysis that all the anhydride had been converted to the half ester.

The esterification in Examples 2 and 3 was also performed in the absence of lithium carbonate catalyst. The same procedure was used except that the heating period was extended to ten hours.

EXAMPLE 4.

A hair spray composition having the following ingredients was prepared:

Component	Amount	
Half ethyl ester of poly(<i>n</i> -butyl vinyl ether/maleic anhydride) neutralized with 5 mole percent of 2-amino-2-methyl-1,3-propanediol	2%	110
SD A—40 denatured ethyl alcohol	48%	
"Freon" 11	25%	115
"Freon" 12	25%	

The above aerosol spray composition was sprayed on human hair with the results shown in Table 1. Even without using a perfume, the above aerosol spray composition did not have an objectionable odour.

The above aerosol spray composition was also sprayed on glass to form a 0.003 inch

film. The results of this test are listed in Table 2.

EXAMPLE 5.

5 An aerosol spray composition was prepared as follows:

	Component	Amount
10	Half ethyl ester of poly(<i>iso</i> -butyl vinyl ether/maleic anhydride) neutralized with 5% of 2-amino-2-methyl-1,3-propanediol	2%
15	SD A—40 denatured ethyl alcohol	48%
	"Freon" 11	25%
	"Freon" 12	25%

20 When sprayed on human hair, the above composition had no objectionable odour and produced the results shown in Table 1. This aerosol composition was also sprayed on a glass plate to form a film 0.003 inch thick, the results being listed in Table 2.

COMPARATIVE EXAMPLE 1.

An aerosol spray composition was prepared as follows:

	Component	Amount	
25	<i>n</i> -Butyl half ester of poly-(methyl vinyl ether/maleic anhydride) neutralized with 5% of 2-amino-2-methyl-1,3-propanediol	2%	30
	SD A—40 denatured ethyl alcohol	48%	
	"Freon" 11	25%	
	"Freon" 12	25%	

35 When sprayed on human hair, the above composition had a definite unpleasant odour and produced the results shown in Table 1. This aerosol composition was also sprayed on a glass plate to form a 0.003 inch film, the results being listed in Table 2. 40

TABLE 1

Hair Holding Studies	Comparative Example 1	Example 4	Example 5
Stiffness	Very good	Good	Very good
Curl snap	Very good	Good	Very good
Comb drag	Moderate	Slight	Slight
Residue on comb	Moderate	Slight	Slight
Residue on hair after combing	Slight	None	Very slight
Manageability	Good	Good	Good

TABLE 2

.003" Film on Glass	Comparative Example 1	Example 4	Example 5
Clarity	Slightly hazy	Clear	Clear
Gloss	Moderate	High	High
Flexibility	Flexible, tough	Flexible, softer than Comp. Ex. 1	Flexible, softer than Comp. Ex. 1
Tackiness			
Dry finger 50% relative humidity, 73°F.	Dry	Dry	Dry
Damp finger	Dry	Dry	Dry
Hardness No. 25 pencil	Marks	Marks	Deep Marks
Water Spotting			
Immediate appearance	Cloudy	Clear	Clear
Dispersibility in Water	Difficult, rubbery	Very difficult	Very difficult
Appearance on redrying	Hazy	Slightly hazy	Clear
Washability of film- water	Difficult	Difficult	Difficult
Washability of film- shampoo	Easy	Very Easy	Very Easy

As is apparent from the results shown in Table 1 and 2, the half esters of poly(*n*-butyl or isobutyl vinyl ether/maleic anhydride) have equivalent or better holding and film-forming properties to another well-known film-forming resin useful in hair sprays. The novel half esters of this invention do not have the objectionable odour of the prior art resins.

EXAMPLE 6.
An aerosol spray composition was prepared as follows:

Component	Amount
Half ethyl ester of <i>n</i> -butyl vinyl ether/maleic anhydride copolymer neutralized with 10 mol percent of triisopropanol amine	2%
Water	48%
"Freon" 11	25%
<i>n</i> -Butane	25%

The above composition when sprayed on hair and on glass film had substantially the same properties as the compositions listed in Tables 1 and 2. This composition also had no objectionable odour.

EXAMPLE 7.

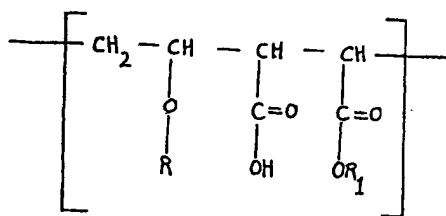
A hair spray composition was prepared as follows:

Component	Amount	
Half ethyl ester of poly <i>iso</i> -butyl vinyl ether/maleic anhydride neutralized with 5 mole percent of 2-amino-2-methyl-1,3-propanediol	3%	35
SD A-40 denatured ethyl alcohol	30%	
Water	17%	
"Freon" 11	25%	
"Freon" 114	25%	40

When this composition was sprayed on hair and on glass it had substantially the same properties as those compositions of Examples 4 and 5 listed in Tables 1 and 2. The above composition also did not have an objectionable odour.

WHAT WE CLAIM IS:—

1. A cosmetic composition comprising a solvent base selected from water, lower aliphatic (C_1 — C_6) monohydric alcohol, and a water-lower aliphatic (C_1 — C_6) monohydric alcohol mixture, and a film-forming copolymer having the following repeating structural unit:



wherein R is *n*-butyl or *isobutyl* and R₁ is methyl or ethyl.

2. The cosmetic composition according to Claim 1, wherein the film-forming copolymer is the half ethyl ester of poly(*n*-butyl vinyl ether/maleic anhydride).

3. The cosmetic composition of Claim 1, wherein the film-forming copolymer is the half ethyl ester of poly(*isobutyl* vinyl ether/maleic anhydride).

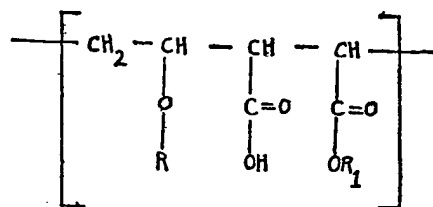
4. The cosmetic composition of any preceding claim, further containing an aerosol propellant.

5. The cosmetic composition of Claim 1, wherein the mixture of water and lower aliphatic (C₁—C₈) monohydric alcohol contains aliphatic monohydric alcohol in a proportion of 30% to 70% by weight, and water in the proportion of 0 to 25% by weight, an aerosol propellant being present in a proportion of 25% to 65% by weight, and the film-forming copolymer being present in a proportion of 0.1% to 5% by weight.

6. The cosmetic composition of Claim 5, wherein the film-forming copolymer is neutralized by from 0.1% to 5% by weight of a neutralizing agent selected from hydroxy substituted alkyl amines.

7. The cosmetic composition of Claim 5 or Claim 6, which additionally contains one or more components selected from organic solvents, perfumes, plasticizers, surfactants, and silicone lubricity agents.

8. A process for spraying hair comprising spraying on the hair an aerosol hair spray composition containing a copolymer having the following repeating structural unit:



wherein R is *n*-butyl or *isobutyl* and R₁ is methyl or ethyl as the film-forming polymer.

9. The process of Claim 8, wherein the film-forming polymer is the ethyl half ester of poly(*n*-butyl vinyl ether/maleic anhydride).

10. The process of Claim 8, wherein the film-forming polymer is the ethyl half ester of poly(*isobutyl* vinyl ether/maleic anhydride).

11. A cosmetic composition according to Claim 1, substantially as herein described and exemplified.

12. A process according to Claim 8 substantially as herein described and exemplified.

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